THE SPECIFIC HEAT OF AN ANISOTROPIC SURFACE

Stephen L. Cunningham[*]
Physics Department
University of California
Irvine, California 92664

ABSTRACT

A Green's function method is used to find the low temperature change in the specific heat due to a (110) surface on a simple cubic monatomic lattice. Two separate first neighbor force constant models are used for the calculation: the first assumes that the atomic motion normal to the surface is uncoupled from motion parallel to the surface; the second is the familiar two force constant model popularized by Montroll and Potts . Both models are anisotropic in the surface and neither satisfies the condition of rotational invariance. Analytic expressions are found for the surface mode dispersion relations and for the low temperature specific heat. It is found that for small deviations from isotropy, the change in the specific heat is independent of the model and is the same for the (110) and (100) surfaces.
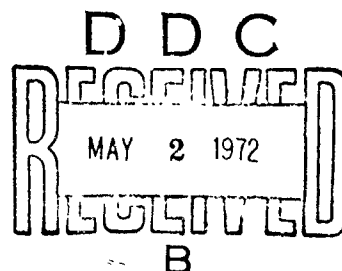
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13 ABSTRACT

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THE SPECIFIC HEAT OF AN ANISOTROPIC SURFACE

There have been a number of studies of the change in the specific heat due to the presence of a surface from both the continuum and the discrete lattice points of view.[1] In every study for which an analytic result is obtained, however, the calculation has been restricted to force models that are either isotropic in the bulk of the crystal or isotropic in the plane of the surface.

In this paper, we will obtain the change in the specific heat due to a (110) surface on a simple cubic monatomic lattice. The lattice will be described by two models, both of which use two first neighbor force constants. The major interest in these calculations comes from the fact that the two models used are anisotropic in the (110) surface and from the fact that the models are sufficiently simple for the entire calculation to be carried out analytically. The models have the disadvantage, however, that they do not satisfy rotational invariance and therefore the results must be interpreted accordingly.

I. SURFACE MODES

. The Cartesian coordinate system will be situated s... that the $\hat{x}$ and $\hat{y}$ unit vectors lie in the plane of the surface (s.. Figure 1). In the harmonic approximation, the force on the 0th atom is:

$$F_\alpha(0) = m\ddot{u}_\alpha(0) = -\sum_{\ell\beta} \phi_{\alpha\beta}(0\ell)u_\beta(\ell) \tag{1.1}$$

where m is the mass of each atom and $u_\alpha(\ell)$ is the displacement from equilibrium of the ℓth atom in the α-Cartesian direction. The particular crystal models to be considered are determined by specifying the values of the force constants $\phi_{\alpha\beta}(0\ell)$. In this paper, the force constants $\phi_{\alpha\beta}(0\ell)$ are zero unless the index ℓ refers to one of the six nearest neighbors of the 0th atom. The labelling we will use for four of these neighbors is shown in Figure 1. Atoms labelled 5 and 6 are located at $\pm a_0(1,0,0)$.

A. Model I, Equations of Motion

The first model to be considered involves central and non-central nearest neighbor forces defined such that the motion of the ions in any one of the Cartesian directions is uncoupled from the motion in any other direction. The equations of motion for a bulk atom in this model are:

$$m\ddot{u}_x(0) = \delta[u_x(5)+u_x(6)-2u_x(0)]+\beta[u_x(1)+u_x(2)+u_x(3)+u_x(4)-4u_x(0)]$$

$$m\ddot{u}_y(0) = \beta[u_y(5)+u_y(6)-2u_y(0)]+\alpha[u_y(1)+u_y(2)+u_y(3)+u_y(4)-4u_y(0)]$$

$$m\ddot{u}_z(0) = \beta[u_z(5)+u_z(6)-2u_z(0)]+\alpha[u_z(1)+u_z(2)+u_z(3)+u_z(4)-4u_z(0)]$$

$$\tag{1.2}$$

The coefficient β is the non-central force constant defining the restoring force when the atoms in the bond are displaced perpendicular to the bond direction. The coefficient δ is the central force constant for the bonds extending in the x-direction. The force constants δ and β are related to the elastic constants by:

$$\delta = a_o C_{11}$$

$$\beta = a_o C_{44} = -a_o C_{12} \tag{1.3}$$

and the force constant α is:

$$\alpha = \frac{1}{2}(\delta + \beta) \tag{1.4}$$

These relations result from identifying the equations of motion in the long wavelength limit with the Christoffel equations of elasticity.

The interest in this very simple model stems from the fact that it gives rise to Rayleigh waves that are split off from the bulk modes even though the motion of the ions normal to the surface is completely uncoupled from the motion of the ions parallel to the surface. This supports the previous observation[2,3] that a sufficient criterion for the presence of Rayleigh waves is that the cut bonds be oblique to the surface.

B. Model II, Equations of Motion

The second model is the now familiar model first suggested by Rosenstock and Newell[4] (and made popular by Montroll and Potts[5]). This model uses two force constants: a central force constant γ which gives the restoring force when the atoms in a bond are displaced in the direction of the bond, and a non-central force constant

λ which gives the restoring force when the displacements are perpendicular to the bond. Due to our choice of coordinate axes, these force constants lead to a coupling of the equations of motion in the y and z direction. The equations of motion for a bulk atom in this model are:

$$m\ddot{u}_x(0) = \gamma[u_x(5)+u_x(6)-2u_x(0)] + \lambda[u_x(1)+u_x(2)+u_x(3)+u_x(4)-4u_x(0)]$$

$$m\ddot{u}_y(0) = \lambda[u_y(5)+u_y(6)-2u_y(0)] + \tfrac{1}{2}(\gamma-\lambda)[u_z(1)-u_z(2)+u_z(3)-u_z(4)]$$

$$+ \tfrac{1}{2}(\gamma+\lambda)[u_y(1)+u_y(2)+u_y(3)+u_y(4)-4u_y(0)]$$

$$m\ddot{u}_z(0) = \lambda[u_z(5)+u_z(6)-2u_z(0)]+ \tfrac{1}{2}(\gamma-\lambda)[u_y(1)-u_y(2)+u_y(3)-u_y(4)]$$

$$+ \tfrac{1}{2}(\gamma+\lambda)[u_z(1)+u_z(2)+u_z(3)+u_z(4)-4u_z(0)] \tag{1.5}$$

The force constants and elastic constants are related by:

$$\gamma = a_o C_{11}$$
$$\lambda = a_o C_{44} = - a_o C_{12} \tag{1.6}$$

The interest in this model is partly pedagogical and partly due to the ability to compare our specific heat results with the same model calculation for the (100) surface.[1,6]

We assume for both models that the displacements of the atoms can be written as:

$$u_\alpha(l) = U_\alpha \exp[i\underset{\sim}{k}\cdot\underset{\sim}{x}(l)+ i\omega t] \tag{1.7}$$

where ω is the angular frequency and $\underset{\sim}{k}$ is the wave vector. To obtain the dispersion relations for the bulk modes, we make the usual assumption of cyclic boundary conditions in the three

Cartesian directions.

By substituting Equation (1.7) into the equations of motion
for the two models, we obtain matrix equations of the form

(Model I)

$$
\begin{bmatrix}
D_{xx}^{(I)} - m\omega^2 & 0 & 0 \\
0 & D_{yy}^{(I)} - m\omega^2 & 0 \\
0 & 0 & D_{yy}^{(I)} - m\omega^2
\end{bmatrix}
\begin{bmatrix}
U_x \\
U_y \\
U_z
\end{bmatrix} = 0
$$

(1.8)

(Model II)

$$
\begin{bmatrix}
D_{xx}^{(II)} - m\omega^2 & 0 & 0 \\
0 & D_{yy}^{(II)} - m\omega^2 & D_{yz}^{(II)} \\
0 & D_{yz}^{(II)} & D_{yy}^{(II)} - m\omega^2
\end{bmatrix}
\begin{bmatrix}
U_x \\
U_y \\
U_z
\end{bmatrix} = 0
$$

(1.9)

It is easily seen that the eigenvectors which diagonalize the
above matrices are independent of the value of the wave vector
and are given by:

(Model I)

$$
e_\alpha^{(I)}(\underset{\sim}{k}j) =
\begin{bmatrix}
1 & 0 & 0 \\
0 & 1 & 0 \\
0 & 0 & 1
\end{bmatrix}
$$

(1.10)

(Model II)

$$
e_\alpha^{(II)}(\underset{\sim}{k}j) = \frac{\sqrt{2}}{2}
\begin{bmatrix}
\sqrt{2} & 0 & 0 \\
0 & 1 & -1 \\
0 & 1 & 1
\end{bmatrix}
$$

(1.11)

The diagonalized matrix elements when set equal to zero give the frequencies of the bulk modes. These are:

(Model I)

$$m\omega_1^2(\underset{\sim}{k}) = D_{xx}^{(I)} = \delta D_1(\underset{\sim}{k}) + \beta D_2(\underset{\sim}{k})$$

$$m\omega_{2,3}^2(k) = D_{yy}^{(I)} = \beta D_1(\underset{\sim}{k}) + \alpha D_2(\underset{\sim}{k})$$

(1.12)

(Model II)

$$m\omega_1^2(\underset{\sim}{k}) = D_{xx}^{(II)} = \gamma D_1(\underset{\sim}{k}) + \lambda D_2(\underset{\sim}{k})$$

$$m\omega_2^2(\underset{\sim}{k}) = D_{yy}^{(II)} - D_{yz}^{(II)}$$

$$= \lambda D_1(\underset{\sim}{k}) + \tfrac{1}{2}(\gamma+\lambda)D_2(\underset{\sim}{k}) - \tfrac{1}{2}(\gamma-\lambda)D_3(\underset{\sim}{k})$$

$$m\omega_3^2(\underset{\sim}{k}) = D_{yy}^{(II)} + D_{yz}^{(II)}$$

$$= \lambda D_1(\underset{\sim}{k}) + \tfrac{1}{2}(\gamma+\lambda)D_2(\underset{\sim}{k}) + \tfrac{1}{2}(\gamma-\lambda)D_3(\underset{\sim}{k})$$

(1.13)

where:

$$D_1(\underset{\sim}{k}) = 2(1 - \cos k_x a_o)$$

$$D_2(\underset{\sim}{k}) = 4(1 - \cos \tfrac{1}{2} k_y a_1 \cos \tfrac{1}{2} k_z a_1)$$

$$D_3(\underset{\sim}{k}) = 4 \sin \tfrac{1}{2} k_y a_1 \sin \tfrac{1}{2} k_z a_1$$

(1.14)

and $\quad a_1 = \sqrt{2}\, a_o$ (1.15)

For comparison with the surface modes, we set the component $k_z = 0$ to obtain the dispersion relations for the bulk modes that propagate parallel to the surface. This gives:

(Model I, bulk)

$$m\omega_1^2(k_x k_y) = 2\delta(1 - \cos k_x a_o) + 4\beta(1 - \cos \tfrac{1}{2} k_y a_1)$$

$$m\omega_{2,3}^2(k_x k_y) = 2\beta(1 - \cos k_x a_o) + 4\alpha(1 - \cos \tfrac{1}{2} k_y a_1)$$

(1.16)

(Model II, bulk)

$$m\omega_1^2(k_x k_y) = 2\gamma(1 - \cos k_x a_o) + 4\lambda(1 - \cos \tfrac{1}{2} k_y a_1)$$

$$m\omega_{2,3}^2(k_x k_y) = 2\lambda(1 - \cos k_x a_o) + 2(\gamma+\lambda)(1 - \cos \tfrac{1}{2} k_y a_\perp)$$

$$(1.17)$$

These dispersion relations are shown in Figure 2.

The models we have chosen are sufficiently simple that the dispersion relations for the surface modes can be determined by either a direct boundary value calculation[7] or a Green's function approach.[8] The mathematical steps for the Green's function method are the more cumbersome, however, and therefore we will defer to the boundary value method in this section.

As indicated in Figure 1, we will assume the crystal occupies the half-space where $z > 0$. Thus, we will assume periodic boundary conditions in the x and y directions, but replace the boundary condition in the z direction by the requirement that the sum of all forces between the atoms on opposite sides of the surface must vanish. For our models, these are the forces on atom 0 due to atoms 1 and 2.

C. Model I, Boundary Conditions

The boundary conditions for Model I can be written:

$$F_x = 0 = \beta[u_x(1) + u_x(2) - 2u_x(0)]$$

$$F_y = 0 = c[u_y(1) + u_y(2) - 2u_y(0)]$$

$$F_z = 0 = \alpha[u_z(1) + u_z(2) - 2u_z(0)] \qquad (1.18)$$

Since the x, y, and z atomic displacements in this model are independent, these boundary conditions are satisfied by displacements of the form (1.7). Upon substitution, we obtain the same complex equation for each condition in (1.18); namely:

$$e^{i\frac{1}{2}k_z a_1} = \cos \tfrac{1}{2} k_y a_1 \tag{1.19}$$

By writing k_z in the form:

$$k_z = k_z^r + ik_z^i \tag{1.20}$$

where k_z^r and k_z^i are real, Equation (1.19) reduces to:

$$k_z^r a_1 = 0$$

$$e^{-k_z^i a_1} = \tfrac{1}{2}(1 + \cos k_y a_1) \tag{1.21}$$

These relationships are shown graphically in Figure 3. The imaginary component k_z^i (called the attenuation coefficient) leads to an amplitude of vibration in Equation (1.7) which varies exponentially with increasing distance from the surface. Solutions where k_z^i is positive are classified as surface waves.

The dispersion curves for the surface modes are found by substituting the value of the wave vector component k_z imposed by the boundary conditions (1.18) into Equations (1.12). This gives the simple result:

(Model I, surface)

$$m\omega_1^2(k_x k_y) = 2\delta(1 - \cos k_x a_0) + \beta(1 - \cos k_y a_1)$$

$$m\omega_{2,3}^2(k_x k_y) = 2\beta(1 - \cos k_x a_0) + \alpha(1 - \cos k_y a_1) \tag{1.22}$$

These dispersion curves are shown in Figure 2. Of interest is to note that for small values of the wave vector $\underset{\sim}{k}$, the dispersion curves for the surface modes and for the bulk modes are the same to order k^4. Hence, the velocities of sound for the surface modes are the same as the velocities of sound for the bulk modes having the same polarization and propagation direction.

D. Model II, Boundary Conditions

The boundary conditions for Model II can be written:

$$F_x = 0 = \lambda[u_x(1) + u_x(2) - 2u_x(0)]$$

$$F_y = 0 = \tfrac{1}{2}(\gamma+\lambda)[u_y(1) + u_y(2) - 2u_y(0)] + \tfrac{1}{2}(\gamma-\lambda)[u_z(1) - u_z(2)]$$

$$F_z = 0 = \tfrac{1}{2}(\gamma+\lambda)[u_z(1) + u_z(2) - 2u_z(0)] + \tfrac{1}{2}(\gamma-\lambda)[u_y(1) - u_y(2)]$$

$$(1.23)$$

For this model, x-displacements of the atoms are independent of the y and z displacements. By substituting displacements of the form (1.7) into the equation for the x component of the force, we obtain Equation (1.19) relating the wave vector components k_y and k_z. For this particular mode, the steps are exactly the same as those for Model I, and hence we obtain for the surface mode:

(Model II, surface)

$$m\omega_1^2(k_x k_y) = 2\gamma(1 - \cos k_x a_0) + \lambda(1 - \cos k_y a_1) \qquad (1.24)$$

Upon substituting Equation (1.7) into the boundary conditions for the y and z component of the force, we obtain two coupled equations in the Fourier coefficients U_y and U_z. In matrix form these are:

$$\begin{bmatrix} (\gamma+\lambda)[\cos \tfrac{1}{2} k_y a_1 - e^{i\frac{1}{2}k_z a_1}] & -i(\gamma-\lambda)\sin \tfrac{1}{2} k_y a_1 \\ -i(\gamma-\lambda)\sin \tfrac{1}{2} k_y a_1 & (\gamma+\lambda)[\cos \tfrac{1}{2} k_y a_1 - e^{i\frac{1}{2}k_z a_1}] \end{bmatrix} \begin{bmatrix} U_y \\ U_z \end{bmatrix} = 0 \tag{1.25}$$

Upon setting the determinant of this 2x2 matrix equal to zero, we find the condition on k_z to be:

$$e^{i\frac{1}{2}k_z a_1} = \cos \tfrac{1}{2} k_y a_1 \pm i \frac{(\gamma-\lambda)}{(\gamma+\lambda)} \sin \tfrac{1}{2} k_y a_1 \tag{1.26}$$

By dividing the wave vector component k_z into its real and imaginary parts as in (1.20) we obtain:

$$e^{-k_z^i a_1} = \frac{\gamma^2 + \lambda^2 + 2\gamma\lambda \cos k_y a_1}{(\gamma+\lambda)^2} \tag{1.27}$$

and

$$\tan \tfrac{1}{2} k_z^r a_1 = \pm \frac{(\gamma-\lambda)}{(\gamma+\lambda)} \tan \tfrac{1}{2} k_y a_1 \tag{1.28}$$

In expressions (1.26) and (1.28), the + (-) sign belongs with the mode $j = 2$ (3).

Ordinarily when two components of the motion are coupled, the form of the displacements which must be used to satisfy the boundary conditions is not Equation (1.7) but rather a linear combination of the type:

$$u_\alpha(\ell) = \sum_{j=2,3} U_\alpha^j \exp[i k^j \cdot x(\ell) + i\dot{\omega} t] \tag{1.29}$$

where the label j is added since the quantities U_α and k may differ for the two modes. This procedure has been fully illustrated by Gazis, Herman, and Wallis.[7] The models used in this paper, however,

are sufficiently simple that the equation that results from this linear combination is a perfect square of the determinant of the matrix in Equation (1.25). Thus the straightforward calculation shown above gives the same results for the two coupled modes as the more involved method.

Since the real part of k_z is not zero for these two modes, they are properly classified as generalized Rayleigh waves. The dependence of k_z upon k_y is shown in Figure 3. Of interest is the fact that the attenuation coefficient k_z^i increases with k_y to a finite value at the zone boundary, whereas for the previous cases, the attenuation coefficient increased without bound. For the vibrational modes that have an infinite attentuation coefficient, only the atom in the surface layer are displaced from equilibrium.

The surface mode frequencies are obtained by substituting the condition (1.26) into the frequency expressions (1.13) for the bulk modes. The result is two degenerate modes whose frequencies are given by:

(Model II, surface)

$$m\omega_{2,3}^2(k_x k_y) = 2\lambda(1-\cos k_x a_0) + \frac{2\gamma\lambda}{(\gamma+\lambda)}(1-\cos k_y a_1) \qquad (1.30)$$

The polarizations of the degenerate modes for both models are given by the eigenvector components in (1.10) and (1.11). An unusual feature of both models is the fact that we obtain three separate surface mode branches corresponding to the three different polarizations of the atomic motion. In continuum calculations, for instance, only one Rayleigh wave is obtained.

The surface mode dispersion relations for Model II have been found previously[9] and are shown in Figure 2. The solution for Model I and Model II are identical in the isotropic limit when $\gamma=\lambda$ and $\zeta=\beta$, but they diverge for other values of the force constants.

II. THE SPECIFIC HEAT

As in the surface mode calculation, the low temperature specific heat due to the surface perturbation can be found in two ways. One method deals with the explicit determination of the surface modes and the perturbed bulk modes prior to calculating the specific heat.[3] The second method sidesteps the problem of determining the perturbed modes by using a Green's function approach. Since the Green's function method is particularly convenient for low temperature calculations where the long wavelength expressions for frequency can be used, we will apply this second method to our present problem.

The method we will follow is that reported by Maradudin and Ashkin[10] and presented fully by Maradudin and Wallis[11] (hereafter referred to $\therefore$ MW). The method uses the function $\Omega(y^2)$ which is defined as

$$\Omega(y^2) = \sum_{\underset{\sim}{k}j} \left\{ \frac{1}{y^2+w_j^2(\underset{\sim}{k})} - \frac{1}{y^2+\omega_j^2(\underset{\sim}{k})} \right\} \tag{2.1}$$

where $w_j(\underset{\sim}{k})$ and $\omega_j(\underset{\sim}{k})$ are the frequencies of the normal modes of the crystal with a surface and without a surface, respectively. MW have shown that when the function $\Omega(y^2)$ has a logarithmic singularity in the limit $|y| \to 0$,

$$\lim_{|y| \to 0} \Omega(y^2) \sim -A \log|y| + o(\log|y|) \tag{2.2}$$

then the change in the specific heat, ΔC_V, is given by:

$$\Delta C_V(T) = 6A \ \zeta(3)k_B(k_BT/\hbar)^2 + o(T^2) \tag{2.3}$$

where $\zeta(3)$ is the Riemann zeta function, k_B is Boltzman's constant, and T is the absolute temperature. The specific heat problem then reduces to the problem of determining the coefficient A in (2.2).

MW have shown the general form for the function $\Omega(y^2)$ to be:

$$\Omega(y^2) = - \sum_{\underset{\sim}{k}j} \frac{t(\underset{\sim}{k}j, -\underset{\sim}{k}j, -y^2)}{[y^2 + \omega_j^2(\underset{\sim}{k})]^2} \tag{2.4}$$

where the term $t(\underset{\sim}{k}j, -\underset{\sim}{k}j, -y^2)$ is the solution of the integral equation:

$$t(\underset{\sim}{k}j, \underset{\sim}{k}'j', -y^2) = V(\underset{\sim}{k}j, \underset{\sim}{k}'j', -y^2)$$

$$- \sum_{\underset{\sim}{k}''j''} \frac{V(\underset{\sim}{k}j, -\underset{\sim}{k}''j'', -y^2)}{y^2 + \omega_{j''}^2(\underset{\sim}{k}'')} \ t(\underset{\sim}{k}''j'', \underset{\sim}{k}'j', -y^2) \tag{2.5}$$

and where:

$$V(\underset{\sim}{k}j, -\underset{\sim}{k}'j', -y^2) = \frac{1}{mL_z} \delta(k_x' - k_x) \delta(k_y' - k_y)$$

$$\times \sum_{\alpha\beta\ell} e_\alpha(\underset{\sim}{k}j) \phi_{\alpha\beta}(0\ell) e_\beta(-\underset{\sim}{k}'j') \delta_{\ell_z + 1}$$

$$\times [1 - e^{i\underset{\sim}{k}\cdot\underset{\sim}{x}(\ell)}][1 - e^{-i\underset{\sim}{k}'\cdot\underset{\sim}{x}(\ell)}] \tag{2.6}$$

Here, $\frac{1}{2} L_z a_1$ is the distance between the two crystal surfaces.

The discussion in this section, then, will proceed to: (1) evaluate the term $V(\underset{\sim}{k}j, -\underset{\sim}{k}'j', -y^2)$ for the two models, (2) solve the integral equation in (2.5) for $t(\underset{\sim}{k}j, \underset{\sim}{k}'j', -y^2)$, (3) perform the integration over the Brillouin zone in the long

wavelength limit indicated in Eq. (2.4), and (4) obtain an analytic expression for the coefficient A for both models by taking the limit in Eq. (2.2).

If the eigenvectors $e_\alpha(\underset{\sim}{k}j)$ are independent of the wave vector $\underset{\sim}{k}$, then for a particular value of the index ℓ, the sum over α and β in Eq. (2.6) can be carried out to give:

$$\sum_{\alpha\beta} e_\alpha(\underset{\sim}{k}j)\phi_{\alpha\beta}(0\ell)e_\beta(-\underset{\sim}{k}'j') = \sum_{\alpha\beta} e_\alpha(j)\phi_{\alpha\beta}(0\ell)e_\beta(j')$$

$$\equiv -C_j(\ell)\delta_{jj'} \qquad\qquad (2.7)$$

This result is easily seen to be true since the $\phi_{\alpha\beta}(0\ell)$ matrix has exactly the same form as the dynamical matrix for a given choice of ℓ.

The number of values of the index ℓ is determined by the number of bonds in the perfect crystal that cross the boundary. For our models, this number is two representing the bonds between atoms $0 - 1$ and $0 - 2$. Thus the terms $C_j(\ell)$ become:

(Model I)
$$C_1(1) = C_1(2) = \beta$$
$$C_2(1) = C_2(2) = \alpha$$
$$C_3(1) = C_3(2) = \alpha \qquad\qquad (2.8)$$

(Model II)
$$C_1(1) = C_1(2) = \lambda$$
$$C_2(1) = \lambda \; ; \; C_2(2) = \gamma$$
$$C_3(1) = \gamma \; ; \; C_3(2) = \lambda \qquad\qquad (2.9)$$

Equation (2.6) can now be written:

$$V(\underset{\sim}{k}j, -\underset{\sim}{k}'j', -y^2) = \delta_{jj'}\delta(k_x'-k_x)\delta(k_y'-k_y)\sum_{\ell=1,2} v_\ell(\underset{\sim}{k}j)v_\ell(-\underset{\sim}{k}'j') \qquad (2.10)$$

where:

$$v_\ell(\underset{\sim}{k}j) = 2\left|\frac{C_j(\ell)}{mL_z}\right|^{\frac{1}{2}} e^{i\frac{1}{2}\underset{\sim}{k}\cdot\underset{\sim}{x}(\ell)} \sin\frac{1}{2}\underset{\sim}{k}\cdot\underset{\sim}{x}(\ell) \tag{2.11}$$

Being able to express the $V(\underset{\sim}{k}j, -\underset{\sim}{k}'j', -y^2)$ term in separable form as in (2.10) is an important step in the evaluation of the specific heat. The ability to do this led MW to use a model which contained only central interactions. In our calculation, the fact that the eigenvectors are independent of the wave vector $\underset{\sim}{k}$ allows us to write (2.10) for a wide range of different models.

By substituting the expression (2.10) into Equation (2.5), we obtain the equation:

$$t(\underset{\sim}{k}j, \underset{\sim}{k}'j', -y^2) = \delta(k_x+k_x')\delta(k_y+k_y')\sum_\ell v_\ell(\underset{\sim}{k}j)v_\ell(\underset{\sim}{k}'j')$$

$$- \sum_\ell \sum_{\underset{\sim}{k}''j''} \delta(k_x-k_x'')\delta(k_y-k_y'') \frac{v_\ell(\underset{\sim}{k}j)v_\ell(-\underset{\sim}{k}''j'')}{y^2+\omega_{j''}^2(\underset{\sim}{k}'')} t(\underset{\sim}{k}''j'', \underset{\sim}{k}'j', -y^2)$$

$$\tag{2.12}$$

The solution of this integral equation with separable kernel is straightforward with the result:

$$t(\underset{\sim}{k}j, -\underset{\sim}{k}j, -y^2) = \sum_{\ell\ell'} v_\ell(\underset{\sim}{k}j)[I-M(k_x k_y j, -y^2)]_{\ell\ell'}^{-1} v_{\ell'}(-\underset{\sim}{k}j) \tag{2.13}$$

where:

$$M_{\ell\ell'}(k_x k_y j, -y^2) = -\sum_{k_z} \frac{v_\ell(-\underset{\sim}{k}j)v_{\ell'}(\underset{\sim}{k}j)}{y^2+\omega_j^2(\underset{\sim}{k})} \tag{2.14}$$

Finally, the function $\Omega(y^2)$ in Equation (2.4) becomes:

$$\Omega(y^2) = -\sum_{\underset{\sim}{k}j} \sum_{\ell\ell'} \frac{v_\ell(\underset{\sim}{k}j)v_{\ell'}(-\underset{\sim}{k}j)}{[y^2+\omega_j^2(\underset{\sim}{k})]^2} [I-M(k_x k_y j, -y^2)]_{\ell\ell'}^{-1} \tag{2.15}$$

Strictly speaking, our choice of a non-primitive unit cell for this problem leads to six phonon branches in the first Brillouin zone as shown in Figure 2. The optical phonon branches, however, are extensions of the acoustic phonon branches from the neighboring zone. This means that by using an extended zone scheme we can treat the problem as if there are only three independent phonon branches. Therefore the sum over wave vector k and branch index j can be converted to integrals as:

$$\sum_{k} \sum_{j=1}^{6} \rightarrow \frac{S_o L_z a_1}{32\pi^3} \int_{-\pi/a_o}^{\pi/a_o} dk_x \int_{-\pi/a_1}^{\pi/a_1} dk_y \int_{-2\pi/a_1}^{2\pi/a_1} dk_z \sum_{j=1}^{3} \qquad (2.16)$$

where S_o is the surface area of the crystal after the cut is made, and the limits on the integral over k_z indicate the use of the extended zone scheme.

We separate out the sum over j from Equation (2.15) by defining:

$$\Omega(y^2) = \sum_{j=1}^{3} \Omega_j(y^2) \qquad (2.17)$$

Thus we obtain:

$$\Omega_j(y^2) = -\frac{S_o L_z a_1}{32\pi^3} \int_{-\pi/a_o}^{\pi/a_o} dk_x \int_{-\pi/a_1}^{\pi/a_1} dk_y \sum_{\ell\ell'}$$

$$\times J_{\ell\ell'}(k_x k_y j, -y^2)[I - M(k_x k_y j, -y^2)]^{-1}_{\ell\ell'} \qquad (2.18)$$

In this expression we have obsorbed the integral over k_z into the term $J_{\ell\ell'}(k_x k_y j, -y^2)$ as:

$$J_{\ell\ell'}(k_x k_y j, -y^2) = \int_{-2\pi/a_1}^{2\pi/a_1} dk_z \frac{v_\ell(\underset{\sim}{k}j) v_{\ell'}(-\underset{\sim}{k}j)}{[y^2 + \omega_j^2(\underset{\sim}{k})]^2} \qquad (2.19)$$

In terms of integrals the $M(k_x k_y j, -y^2)$ matrix becomes:

$$M_{\ell\ell'}(k_x k_y, -y^2) = -\frac{L_z a_1}{4\pi} \int_{-2\pi/a_1}^{2\pi/a_1} dk_z \frac{v_\ell(-\underset{\sim}{k}j) v_{\ell'}(\underset{\sim}{k}j)}{[y^2 + \omega_j^2(\underset{\sim}{k})]} \qquad (2.20)$$

To determine the long wavelength limit, we expand the relevant expressions in terms of the lattice parameter a_0 and keep only those terms of lowest order. In taking the limit as $a_0 \rightarrow 0$, the density and the elastic constants must remain finite. This implies that the mass m is of order a_0^3 and the force constants are of order a_0^1.

The frequencies of the perfect crystal normal modes in the long wavelength limit can be written:

$$\omega_j^2(\underset{\sim}{k}) = c_{jx}^2 k_x^2 + c_{jy}^2 k_y^2 + c_{jz}^2 k_z^2 \qquad (2.21)$$

where the coefficients $c_{j\alpha}^2$ for each model are found by comparison with Equations (1.12), (1.13), and (1.14) in the longwavelength limit. The matrix of the values $c_{j\alpha}^2$ for Model I is:

(Model I)

$$c_{j\alpha}^2 = \frac{a_0^2}{m} \begin{bmatrix} \delta & \beta & \beta \\ \beta & \alpha & \alpha \\ \beta & \alpha & \alpha \end{bmatrix} \qquad (2.22)$$

For Model II, we have the added complication that the frequency expressions for modes $j = 2,3$ have a term that involves the product of k_y and k_z. In the long wavelength limit, the normal mode frequencies are:

$$m\omega_2^2(\underset{\sim}{k}) = \lambda k_x^2 a_o^2 + \tfrac{1}{4}(\gamma+\lambda)k_y^2 a_1^2 + \tfrac{1}{4}(\gamma+\lambda)k_z^2 a_1^2$$

$$- \tfrac{1}{2}(\gamma-\lambda)k_y a_1 k_z a_1 \tag{2.23a}$$

$$m\omega_3^2(\underset{\sim}{k}) = \lambda k_x^2 a_o^2 + \tfrac{1}{4}(\gamma+\lambda)k_y^2 a_1^2 + \tfrac{1}{4}(\gamma+\lambda)k_z^2 a_1^2$$

$$+ \tfrac{1}{2}(\gamma-\lambda)k_y a_1 k_z a_1 \tag{2.23b}$$

These frequencies can be put into the form (2.21) by a change of variable.

$$j = 2; \quad k_z' a_1 = k_z a_1 - \frac{(\gamma-\lambda)}{(\gamma+\lambda)} k_y a_1$$

$$j = 3; \quad k_z'' a_1 = k_z a_1 + \frac{(\gamma-\lambda)}{(\gamma+\lambda)} k_y a_1 \tag{2.24}$$

with the result:

$$m\omega_2^2(\underset{\sim}{k}) = \lambda k_x^2 a_o^2 + \frac{\gamma\lambda}{(\gamma+\lambda)} k_y^2 a_1^2 + \tfrac{1}{4}(\gamma+\lambda)(k_z' a_1)^2$$

$$m\omega_3^2(\underset{\sim}{k}) = \lambda k_x^2 a_o^2 + \frac{\gamma\lambda}{(\gamma+\lambda)} k_y^2 a_1^2 + \tfrac{1}{4}(\gamma+\lambda)(k_z'' a_1)^2 \tag{2.25}$$

Thus, if we remember for the time being that the wave vector component k_z is different for each mode j, then the $c_{j\alpha}^2$ matrix for Model II is:

(Model II)

$$c_{j\alpha}^2 = \frac{a_o^2}{m} \begin{bmatrix} \gamma & \lambda & \lambda \\ \lambda & \dfrac{2\gamma\lambda}{(\gamma+\lambda)} & \tfrac{1}{2}(\gamma+\lambda) \\ \lambda & \dfrac{2\gamma\lambda}{(\gamma+\lambda)} & \tfrac{1}{2}(\gamma+\lambda) \end{bmatrix} \tag{2.26}$$

In changing the integration variable from k_z to k_z' or k_z'' as in Equations (2.24), the only effect is to add a constant to the integration limits. Before taking the long wavelength limit, the integrand is periodic in the extended zone scheme. Therefore adding a constant to the limits of the integral has no effect on the value of the integral. The same is true in the long wavelength limit provided the new integration limits always span the origin. This last condition is always met for both cases; therefore:

$$\int_{-2\pi/a_1}^{2\pi/a_1} dk_z = \int_{-2\pi/a_1}^{2\pi/a_1} dk_z' = \int_{-2\pi/a_1}^{2\pi/a_1} dk_z'' \tag{2.27}$$

and we can forget the distinction between k_z, k_z', and k_z'' that we made when we wrote the $c_{j\alpha}^2$ matrix in (2.26).

The $J_{\ell\ell'}(k_x k_y j, -y^2)$ matrix elements can be written in the long wavelength limit as:

$$J_{11}(k_x k_y j, -y^2) = -\frac{C_j(1)}{4mL_z} \int_{-2\pi/a_1}^{2\pi/a_1} dk_z \frac{(k_z+k_y)^2 a_1^2}{[d_j^2 + c_{jz}^2 k_z^2]^2}$$

$$J_{22}(k_x k_y j, -y^2) = -\frac{C_j(2)}{4mL_z} \int_{-2\pi/a_1}^{2\pi/a_1} dk_z \frac{(k_z-k_y)^2 a_1^2}{[d_j^2 + c_{jz}^2 k_z^2]^2}$$

$$J_{12}(k_x k_y j, -y^2) = -\frac{[C_j(1)C_j(2)]^{\frac{1}{2}}}{4mL_z} e^{-i\frac{1}{2}k_y a_1}$$

$$\times \int_{-2\pi/a_1}^{2\pi/a_1} dk_z \frac{(k_z^2 - k_y^2) a_1^2}{[d_j^2 + c_{jz}^2 k_z^2]^2} = J_{21}^*(k_x k_y j, -y^2) \tag{2.28}$$

where:

$$d_j^2 = y^2 + c_{jx}^2 k_x^2 + c_{jy}^2 k_y^2 \tag{2.29}$$

These expressions are valid for both models and for all j. The limits of integration can be extended to $\pm \infty$ since the integrands are properly convergent. The terms in the integrand that are odd in k_z vanish, and we obtain:

$$J_{11}(k_x k_y j, -y^2) = -C_j(1)[P + Q k_y^2]$$

$$J_{22}(k_x k_y j, -y^2) = -C_j(2)[P + Q k_y^2]$$

$$J_{12}(k_x k_y j, -y^2) = -[C_j(1) \, C_j(2)]^{\frac{1}{2}}[P - Q k_y^2] \, e^{-i\frac{1}{2}k_y a_1}$$

$$= J_{21}^*(k_x k_y j, -y^2) \tag{2.30a}$$

where:

$$P = \frac{\pi a_o^2}{4mL_z d_j c_{jz}} \left(\frac{1}{c_{jz}^2} \right)$$

$$Q = \frac{\pi a_o^2}{4mL_z d_j c_{jz}} \left(\frac{1}{d_j^2} \right) \tag{2.30b}$$

All matrix elements are of order a_o^0.

The $M_{\ell\ell'}(k_x k_y j, -y^2)$ matrix elements in the long wavelength limit can be written:

$$M_{11}(k_x k_y j, -y^2) = \frac{\sqrt{2} \, a_o C_j(1)}{16\pi m} \int_{-2\pi/a_1}^{2\pi/a_1} dk_z \, \frac{(k_z + k_y)^2 a_1^2}{d_j^2 + c_{jz}^2 k_z^2}$$

$$M_{22}(k_x k_y j, -y^2) = \frac{\sqrt{2}\ a_o C_j(2)}{16\pi m} \int_{-2\pi/a_1}^{2\pi/a_1} dk_z\ \frac{(k_z - k_y)^2 a_1^2}{d_j^2 + c_{jz}^2 k_z^2}$$

$$M_{12}(k_x k_y j, -y^2) = \frac{\sqrt{2}\ a_o [C_j(1) C_j(2)]^{\frac{1}{2}}}{16\pi m}\ e^{i\frac{1}{2}k_y a_1}$$

$$\times \int_{-2\pi/a_1}^{2\pi/a_1} dk_z\ \frac{(k_z^2 - k_y^2) a_1^2}{d_j^2 + c_{jz}^2 k_z^2} = M_{21}^*(k_x k_y j, -y^2) \tag{2.31}$$

Again, these expressions are valid for both models and all j. Some of these integrals do not converge when the limits of integration are extended to $\pm\ \infty$. Hence, we retain finite limits for those integrals that diverge and change the limits of the other integrals to $\pm\ \infty$ to obtain:

$$M_{11}(k_x k_y j, -y^2) = C_j(1)\ [R - S + Tk_y^2]$$

$$M_{22}(k_x k_y j, -y^2) = C_j(2)\ [R - S + Tk_y^2]$$

$$M_{12}(k_x k_y j, -y^2) = [C_j(1) C_j(2)]^{\frac{1}{2}}\ [R - S - Tk_y^2]\ e^{i\frac{1}{2}k_y a_1}$$

$$= M_{21}^*(k_x k_y j, -y^2) \tag{2.32}$$

where:

$$R = \frac{a_o^2}{2mc_{jz}^2}$$

$$S = \frac{\sqrt{2}\ a_o^3 d_j}{8mc_{jz}^3}$$

$$T = \frac{\sqrt{2}\, a_o^3}{8md_j c_{jz}} \tag{2.33}$$

The coefficient R is of order a_o^{-1} whereas S and T are of order a_o^0. All three terms must be retained in the limit of $a_o \to 0$, however, until after the inverse matrix $[I - M(k_x k_y j, -y^2)]_{\mathcal{U}}^{-1}$, is found.

The determinant $\Delta(k_x k_y j, -y^2)$ of the matrix $I - M(k_x k_y j, -y^2)$ is:

$$\Delta(k_x k_y j, -y^2) = 1 - [C_j(1)+C_j(2)]R + 4TRC_j(1)C_j(2)k_y^2$$

$$+ [C_j(1)+C_j(2)][S-Tk_y^2]$$

$$- 4TSC_j(1)C_j(2)k_y^2 \tag{2.34}$$

Of the five terms on the right hand side, the first two are of order 1, the second two are of order a_o^1, and the last is of order a_o^2. The two terms of order 1 when written in full are:

$$1 - [C_j(1)+C_j(2)]\, R = 1 - \frac{a_o\, [C_j(1)+C_j(2)]}{2mc_{jz}^2} \tag{2.35}$$

These terms identically vanish because:

$$c_{jz}^2 = \frac{a_o^2\, [C_j(1)+C_j(2)]}{2m} \tag{2.36}$$

for all j and for both models. Thus, the lowest order of the determinant is a_o^1 and can be written:

$$\Delta(k_x k_y j, -y^2) = \frac{\sqrt{2}\, a_o}{4c_{jz}d_j}\left\{ y^2 + c_{jx}^2 k_x^2 + \tilde{c}_{jy}^2 k_y^2 \right\} \tag{2.37}$$

where:

$$\tilde{c}_{jy}^2 = c_{jy}^2 - \frac{a_o^2 \, [C_j(1) - C_j(2)]^2}{2m \, [C_j(1) + C_j(2)]} \tag{2.38}$$

The lowest order of the inverse matrix, then, is a_o^{-1} and can be written:

$$[I - M(k_x k_y j, -y^2)]_{\ell\ell'}^{-1} = \frac{\begin{bmatrix} C_j(1) & [C_j(1)C_j(2)]^{\frac{1}{2}} e^{i\frac{1}{2}k_y a_1} \\ [C_j(1)C_j(2)]^{\frac{1}{2}} e^{-i\frac{1}{2}k_y a_1} & C_j(2) \end{bmatrix}}{\Delta(k_x k_y j, -y^2) \, [C_j(1) + C_j(2)]} \tag{2.39}$$

The sum of the products of the J matrix elements and the M matrix elements that appear in (2.18) is:

$$\sum_{\ell\ell'} J_{\ell\ell'}(k_x k_y j, -y^2) \, [I - M(k_x k_y j, -y^2)]_{\ell\ell'}^{-1}$$

$$= - \frac{2\pi}{\sqrt{2} L_z a_o \tilde{d}_j^2} \left\{ 1 + \frac{(c_{jy}^2 - \tilde{c}_{jy}^2) k_y^2}{d_j^2} \right\} \tag{2.40}$$

where:

$$\tilde{d}_j^2 = y^2 + c_{jx}^2 k_x^2 + \tilde{c}_{jy}^2 k_y^2 \tag{2.41}$$

The integral in (2.18) for the function $\Omega_j(y^2)$ can now be written in two parts as:

$$\Omega_j(y^2) = \Omega_j^{(1)}(y^2) + \Omega_j^{(2)}(y^2) \tag{2.42}$$

where:

$$\Omega_j^{(1)}(y^2) = \frac{S_o}{16\pi^2} \int_{-\pi/a_o}^{\pi/a_o} dk_x \int_{-\pi/a_1}^{\pi/a_1} dk_y \frac{1}{y^2 + c_{jx}^2 k_x^2 + \tilde{c}_{jy}^2 k_y^2} \tag{2.43}$$

and

$$\Omega_j^{(2)}(y^2) = \frac{S_o(c_{jy}^2 - \tilde{c}_{jy}^2)}{16\pi^2} \int_{-\pi/a_o}^{\pi/a_o} dk_x \int_{-\pi/a_1}^{\pi/a_1} dk_y \frac{k_y^2}{d_j^2 \tilde{d}_j^2} \tag{2.44}$$

For the term $\Omega_j^{(1)}(y^2)$, the limits for the integral over k_y can be extended to $\pm \infty$ and the integration can be carried out directly to give:

$$\Omega_j^{(1)}(y^2) = \frac{S_o}{16\pi \tilde{c}_{jy}} \int_{-\pi/a_o}^{\pi/a_o} dk_x \frac{1}{[y^2 + c_{jx}^2 k_x^2]^{\frac{1}{2}}} \tag{2.45}$$

For this integral, the limits must remain finite until after the integration is performed.

$$\Omega_j^{(1)}(y^2) = \frac{S_o}{16\pi \tilde{c}_{jy} c_{jx}} \left\{ \log\left[k_x + \left(k_x^2 + \frac{y^2}{c_{jx}^2} \right)^{\frac{1}{2}} \right] \Bigg|_{k_x = -\pi/a_o}^{k_x = \pi/a_o} \right\} \tag{2.46}$$

In the limit as $a_o \to 0$, this becomes:

$$\Omega_j^{(1)}(y^2) = -\frac{S_o}{8\pi c_{jx} \tilde{c}_{jy}} \log|y| + \text{constant} \tag{2.47}$$

For the term $\Omega_j^{(2)}(y^2)$, we split the integrand as:

$$\frac{(c_{jy}^2 - \tilde{c}_{jy}^2) k_y^2}{d_j^2 \tilde{d}_j^2} = \frac{1}{y^2 + c_{jx}^2 k_x^2 + \tilde{c}_{jy}^2 k_y^2} - \frac{1}{y^2 + c_{jx}^2 k_x^2 + c_{jy}^2 k_y^2} \tag{2.48}$$

Thus, aside from different coefficients, the resulting two integrals for $\Omega_j^{(2)}(y^2)$ are of exactly the same form as the integral for $\Omega_j^{(1)}(y^2)$ in (2.43). Thus, we obtain directly:

$$\Omega_j^{(2)}(y^2) = -\frac{S_o}{8\pi}\left(\frac{1}{c_{jx}\widetilde{c}_{jy}} - \frac{1}{c_{jx}c_{jy}}\right)\log|y| + \text{constant}$$

(2.49)

By substituting the results (2.47) and (2.49) into Equation (2.17) and comparing with Equation (2.2), we obtain for the term A:

$$A = \frac{S_o}{8\pi}\sum_{j=1,2,3}\frac{1}{c_{jx}\widetilde{c}_{jy}}\left\{1 + \frac{c_{jy}-\widetilde{c}_{jy}}{c_{jy}}\right\}$$

(2.50)

For Model I, the second term in the sum vanishes because the term $\widetilde{c}_{jy} = c_{jy}$ for all j. Thus, by using the identifications in (2.21) and (2.22) we obtain:

(Model I)

$$A = \frac{S_o}{8\pi r c_\ell^2}\left\{1 + \frac{2\sqrt{2}}{(1+r^2)^{\frac{1}{2}}}\right\}$$

(2.51)

where: $\qquad r = \dfrac{c_t}{c_\ell}$ (2.52)

and c_ℓ and c_t are the longitudinal and transverse velocities of sound respectively in the bulk crystal (100) directions.

For Model II, the second term in (2.50) vanishes for the mode j = 1, and is the same for modes j = 2 and j = 3. For this model, the term $\widetilde{c}_{jy}$ is:

$$j=2,3; \quad \widetilde{c}_{jy} = \chi\, c_{jy} = \left[1 - \left(\frac{1-r^2}{2r}\right)^2\right]^{\frac{1}{2}} c_{jy}$$

(2.53)

so that the coefficient A becomes:

(Model II)

$$A = \frac{S_o}{8\pi r c_{\ell}^2} \left\{ 1 + \frac{2(1+r^2)^{\frac{1}{2}}}{\sqrt{2}\, r} \left(\frac{2-\chi}{\chi} \right) \right\}$$ (2.54)

Dobrzynski and Leman[6] calculated the specific heat using Model II for the (100) surface by a different method and obtained the result:

(Model II, (100) surface)

$$A = \frac{S_o}{8\pi r^2 c_{\ell}^2} \left\{ 1 + 2r \right\}$$ (2.55)

In the isotropic limit where $r \to 1$ and $\chi \to 1$, the three results (2.51), (2.54), and (2.55) reduce to:

$$A_{iso} = \frac{3S_o}{8\pi c_{\ell}^2}$$ (2.56)

which agrees with the result of Maradudin et.al.[1]

The value of the coefficient A for the surface of an isotropic solid has been determined from a correct continuum calculation to be:[11]

$$A_{iso} = \frac{S_o}{8\pi c_{\ell}^2} \left(\frac{10}{3} \right)$$ (continuum) (2.57)

The fact that our value of A_{iso} is 10% lower than the continuum value is not too surprising since our models are not rotationally invariant.[12]

For small deviations from isotropy, we introduce the quantity Δ:

$$\Delta = 1 - r$$ (2.58)

To lowest order in Δ, the coefficient A for the three results
(2.51), (2.54), and (2.55) becomes:

$$A = A_{iso} \left(1 + \frac{4}{3} \Delta\right) \tag{2.59}$$

The fact that we find the deviation of the specific heat for small
deviations from isotropy to be independent of the surface and model
for the two surfaces and two models considered supports the belief
that the expressions give meaningful qualitative behavior in this
limit.

III. CONCLUSIONS

(1) We have found the change in the specific heat at low
temperatures due to the (110) surface in a cubic monatomic lattice
for two simple interatomic force constant models to be:

(Model I)

$$\Delta C_v(T) = \frac{3k_B^3 \zeta(3)}{4\pi\hbar^2 rc_\ell^2} \left\{ 1 + \frac{2\sqrt{2}}{(1+r^2)^{\frac{1}{2}}} \right\} S_o T^2 \tag{3.1}$$

(Model II)

$$\Delta C_v(T) = \frac{3k_B^3 \zeta(3)}{4\pi\hbar^2 rc_\ell^2} \left\{ 1 + \frac{2(1+r^2)^{\frac{1}{2}}}{\sqrt{2}\, r} \left(\frac{2-\chi}{\chi}\right) \right\} S_o T^2 \tag{3.2}$$

To our knowledge, this is the first determination of the change
in the specific heat due to a surface that is anisotropic.

(2) We have shown that the (110) surface of a simple cubic
monatomic lattice gives rise to Rayleigh waves that are split off
from the bulk modes for very simple force constant models. The
surface waves arise even for the case where the atomic motion
normal to the surface is totally uncoupled from motion parallel
to the surface. The only condition needed to obtain Rayleigh waves

is that the "bonds" between atoms on opposite sides of the surface be oblique to the surface.

(3) We have provided a second example of the practicality of the Green's function method suggested by Maradulin and Ashkin[10] in calculating the low temperature surface specific heat. The usefulness of the method depends upon the ability to express the resulting integral equation in separable form. Maradudin and Wallis[11] succeeded in doing this by assuming central force interactions. This paper succeeded in doing this by using the fact that the eigenvectors for the assumed models are independent of wave vector.

(4) We have found that the value of the surface specific heat for the two models in the isotropic limit is 10% lower than the value found by correct continuum theory. We believe that this discrepancy is due solely to the fact that the assumed models do not satisfy the rotational invariance condition.

(5) We have shown that as the longitudinal velocity of sound increases relative to the transverse velocity of sound for values that nearly satisfy the isotropy condition, the value of the surface specific heat also increases. This result is independent of the model and surface to first order in the deviation from isotropy for the two models presented and for the (110) and (100) surfaces.

IV. ACKNOWLEDGEMENTS

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FIGURE CAPTIONS

Figure 1: The atomic configuration and unit vector designation for the (110) surface of a simple cubic monatomic lattice. The unit vector $\hat{x}$ is perpendicular to the y-z plane shown and the atoms designated 5 and 6 are located at $\pm \hat{x}a_o$.

Figure 2: The dispersion curves for the bulk and surface phonons propagating in the $\hat{y}$ direction for Model II where the force constants are related by $\gamma = 2\lambda$. The bulk mode dispersion curves for Model I are the same as those shown here if the force constants δ and β are identified with γ and λ respectively. With this identification, the surface mode $j = 1$ is identical for the two models but the degenerate modes $j = 2,3$ are higher for Model I by a factor of $(9/8)^{\frac{1}{2}}$.

Figure 3: The relation between the complex wave vector k_z and the wave vector k_y for Models I and II. The attenuation coefficients for all modes in Model I and for the mode $j = 1$ for Model II are independent of the force constants and diverge as k_y approaches the zone boundary. The real part of the wave vector k_z vanishes for these modes. The real and imaginary parts of k_z for modes $j = 2,3$ in Model II are shown for the case $\gamma = 2\lambda$.
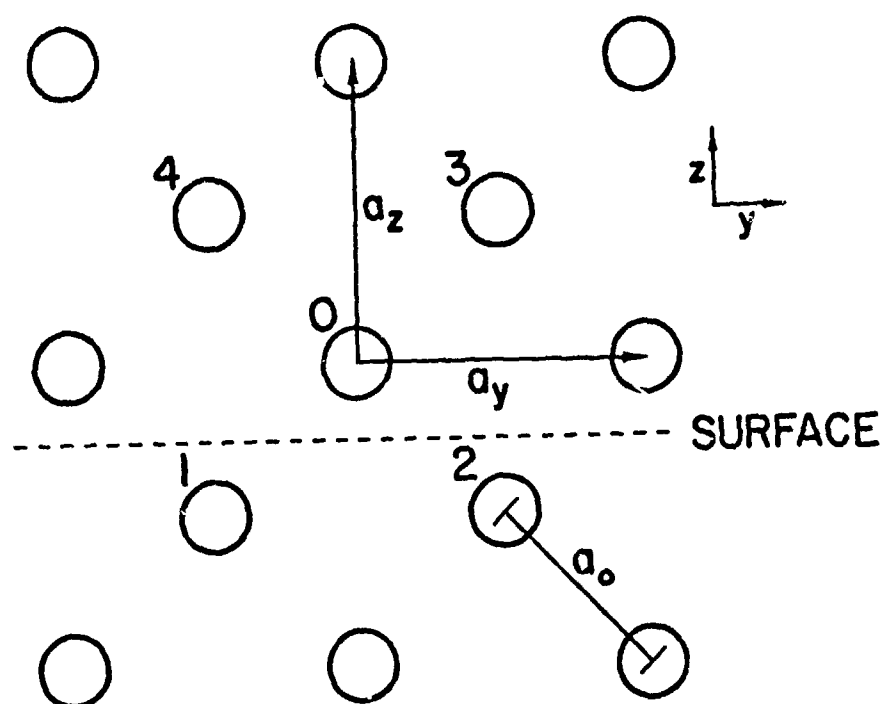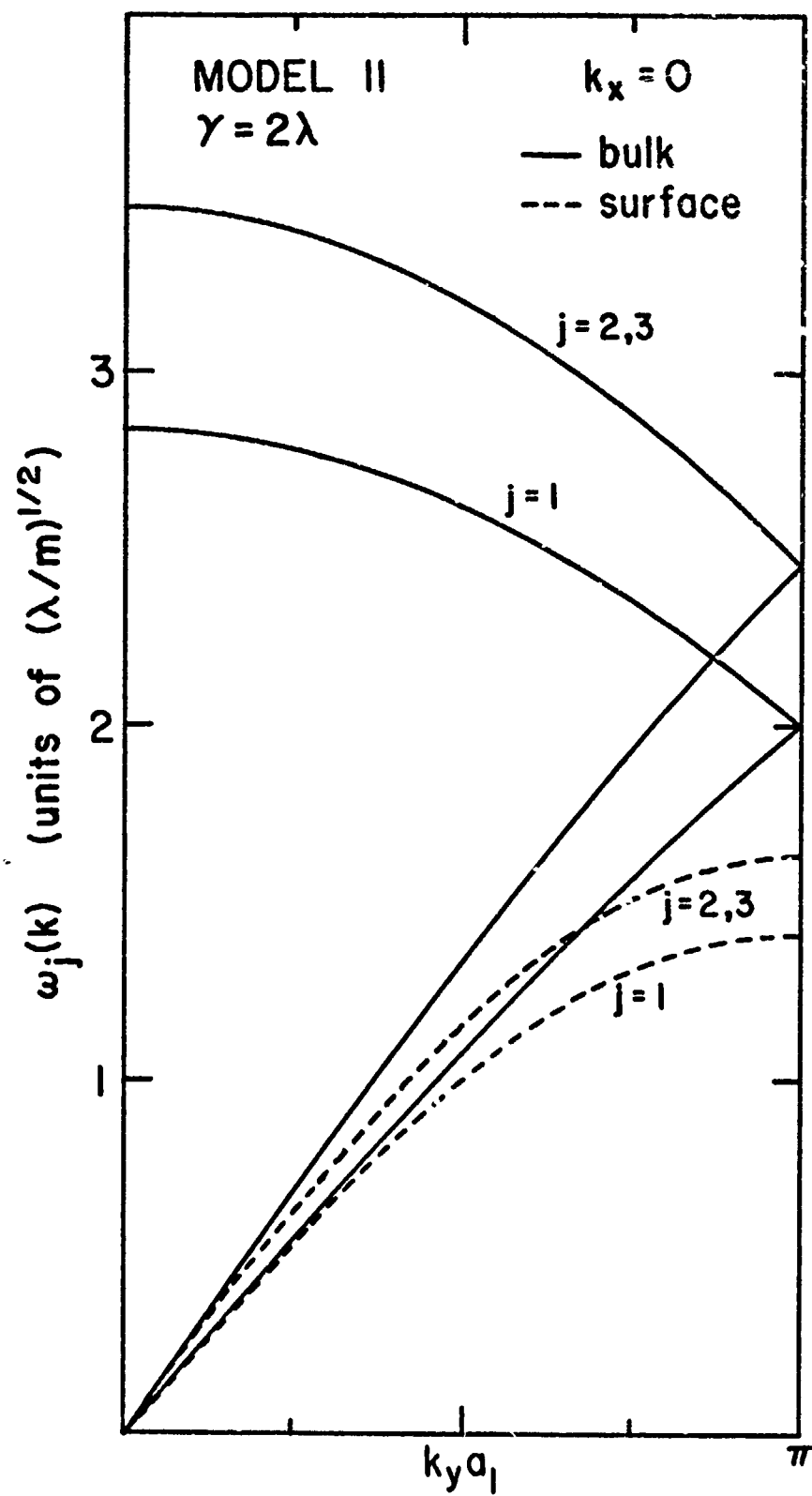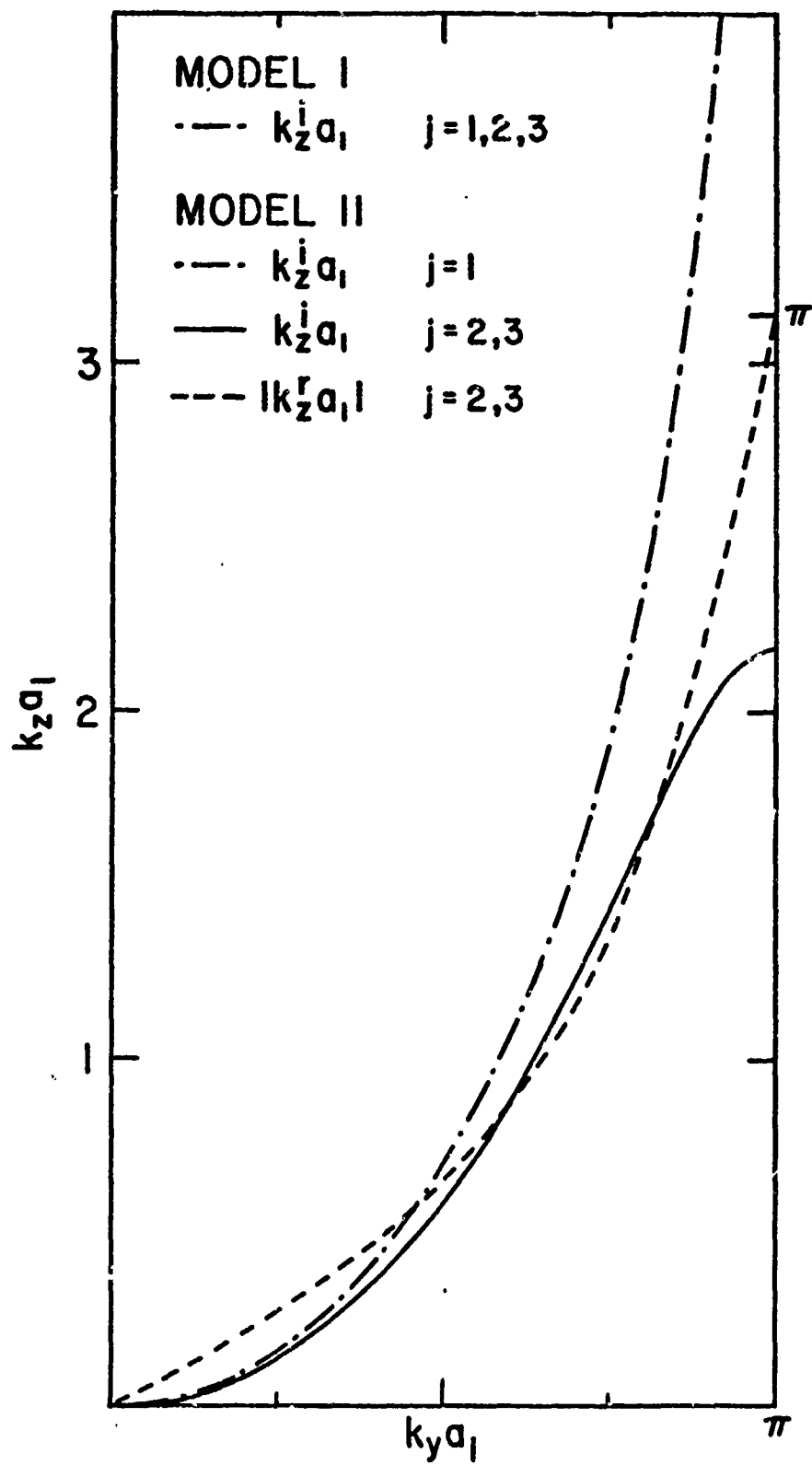
FIG. 1

MODEL II $k_x = 0$
$\gamma = 2\lambda$

bulk
surface

$j = 2,3$

$j = 1$

$j = 2,3$

$j = 1$

$\omega_j(k)$ (units of $(\lambda/m)^{1/2}$)

$k_y a_1$ π

34

FIG. 2

FIG. 3